

5. Mass Transfer with Chemical Reaction

Chlorine absorption into S(IV) solutions occurs by mass transfer with simultaneous chemical reaction. Chlorine must first diffuse from the bulk gas to the gas liquid interface with the flux (N_{Cl_2}) given by:

$$N_{Cl_2} = k_g (P_{Cl_2,b} - P_{Cl_2,i}) \quad (5-1)$$

Then, chlorine absorption into the liquid occurs by mass transfer with fast chemical reaction in the boundary layer with the same flux:

$$N_{Cl_2} = \frac{Ek_{L,Cl_2}^o (P_{Cl_2,i} - P_{Cl_2,b}^*)}{H_{Cl_2}} \quad (5-2)$$

According to surface renewal theory (Danckwerts, 1970), the enhancement factor (E) can be expressed as (Critchfield, 1988; Shen, 1997; Zhao, 1997):

$$E = \sqrt{1 + \frac{D_{Cl_2}}{k_L^o} (k_{1,H_2O} + k_{2,buf} [buffer]_i + k_{2,OH} [OH^-]_i + k_{2,S(IV)} [S(IV)]_i)} \quad (5-3)$$

which incorporates the reactions which contribute to chlorine absorption. If the chlorine/S(IV) reaction is the dominant reaction and equilibrium effects are negligible, then the flux expression simplifies to:

$$N_{Cl_2} = Ek_{L,Cl_2}^o \frac{P_{Cl_2,i}}{H_{Cl_2}} = \frac{P_{Cl_2,i}}{H_{Cl_2}} \sqrt{D_{Cl_2} k_{2,S(IV)} [S(IV)]_i} \quad (5-4)$$

The enhancement factor expression is derived assuming that the chlorine/S(IV) reaction is first order in chlorine and first order in S(IV). If this model is correct, the extracted rate constant, $k_{2,S(IV)}$, can be used to extrapolate chlorine removal at low chlorine concentrations. The corresponding rate expression is:

$$\text{reaction rate} = k_{2,S(IV)} [Cl_2][S(IV)] \quad (5-5)$$

The concentrations, physical properties (diffusivity, D , and Henry's law constant, H) and rate constants for the water and hydroxide reactions are known. At 25°C, the Henry's law constant for chlorine, H_{Cl_2} , was taken to be 16.7 atm-m³/kmol (Brian et al., 1966), and the diffusion coefficient for chlorine through water, D_{Cl_2} , was taken to be 1.48 x 10⁻⁹ m²/s (Spalding, 1962). The chlorine flux was determined experimentally from the gas phase material balance. Thus, the only unknown is the rate constant for the chlorine/S(IV) reaction. This rate constant, $k_{2,S(IV)}$, can be calculated by substituting the enhancement factor into the flux equation (5-2).

The interfacial liquid S(IV) concentration is obtained by assuming that Cl₂ reacts with S(IV) at the gas/liquid interface.

$$N_{Cl_2} = \Phi N_{S(IV)} = \Phi k_{L, S(IV)}^o ([S(IV)]_b - [S(IV)]_i) \quad (5-6)$$

$$[S(IV)]_i = [S(IV)]_b - \frac{N_{Cl_2}}{\Phi k_{L, S(IV)}^o} \quad (5-7)$$

Φ represents the stoichiometric relationship between the reactants. For example, in the reaction $Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O$, $\Phi = 1/2$ since 1 mol of Cl₂ reacts with 2 mol of OH⁻.

The rate constant can only be extracted if mass transfer does not limit the chlorine absorption. When the S(IV) concentration is high relative to the chlorine concentration, the chlorine flux is limited by the resistance in the gas phase, and the flux from Equation 5-1 simplifies to:

$$N_{Cl_2} = k_g P_{Cl_2, b} \quad (5-8)$$

Under these conditions, there is essentially no chlorine at the interface since all the chlorine reacts with S(IV) as soon as the chlorine reaches the interface. Thus, the chlorine absorption only depends on how fast the chlorine diffuses from the bulk gas to the gas/liquid interface, not on the kinetics.

When the chlorine concentration is high relative to the S(IV) concentration, the flux is limited by S(IV) depletion at the interface. This means that there is essentially no S(IV) at the interface since whatever S(IV) diffuses to the interface is readily depleted through reaction with chlorine. Under these conditions, the flux in Equation 5-6 simplifies to:

$$N_{Cl_2} = \Phi N_{S(IV)} = \Phi k_{L, S(IV)}^o [S(IV)]_b \quad (5-9)$$

showing that the flux of chlorine is linear with the bulk S(IV) concentration.

The fraction gas film resistance is a parameter used in analyzing some of the data. The fraction gas film resistance is directly related to reaction kinetics:

$$\frac{K_{OG}}{k_g} = \frac{1}{1 + \frac{k_g H_{Cl_2}}{E k_{L, Cl_2}^o}} = \text{fraction gas film resistance} \quad (5-10)$$

As the enhancement factor (E) increases, which corresponds to fast reaction rates, the total resistance to mass transfer (1/K_{OG}) becomes limited by gas film resistance (1/k_g). Under these conditions, the fraction gas film resistance (5-10) approaches unity and becomes independent of reaction kinetics. Thus, data which approach gas film resistance cannot be used for extracting kinetics. For these data, the gas film mass transfer coefficient (as opposed to kinetics) is being measured.